

[54] **CONVERSION OF A LOWER ALKANE**

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[58] **Field of Search** ..... 585/510, 500, 322, 541, 585/415, 417, 418, 654, 656, 658, 661, 700, 943

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[57] **ABSTRACT**

The catalyzed oxidative coupling of a lower molecular weight alkane to higher molecular weight hydrocarbons which are then oligomerized to form aromatic hydrocarbons is disclosed.

**21 Claims, 1 Drawing Sheet**

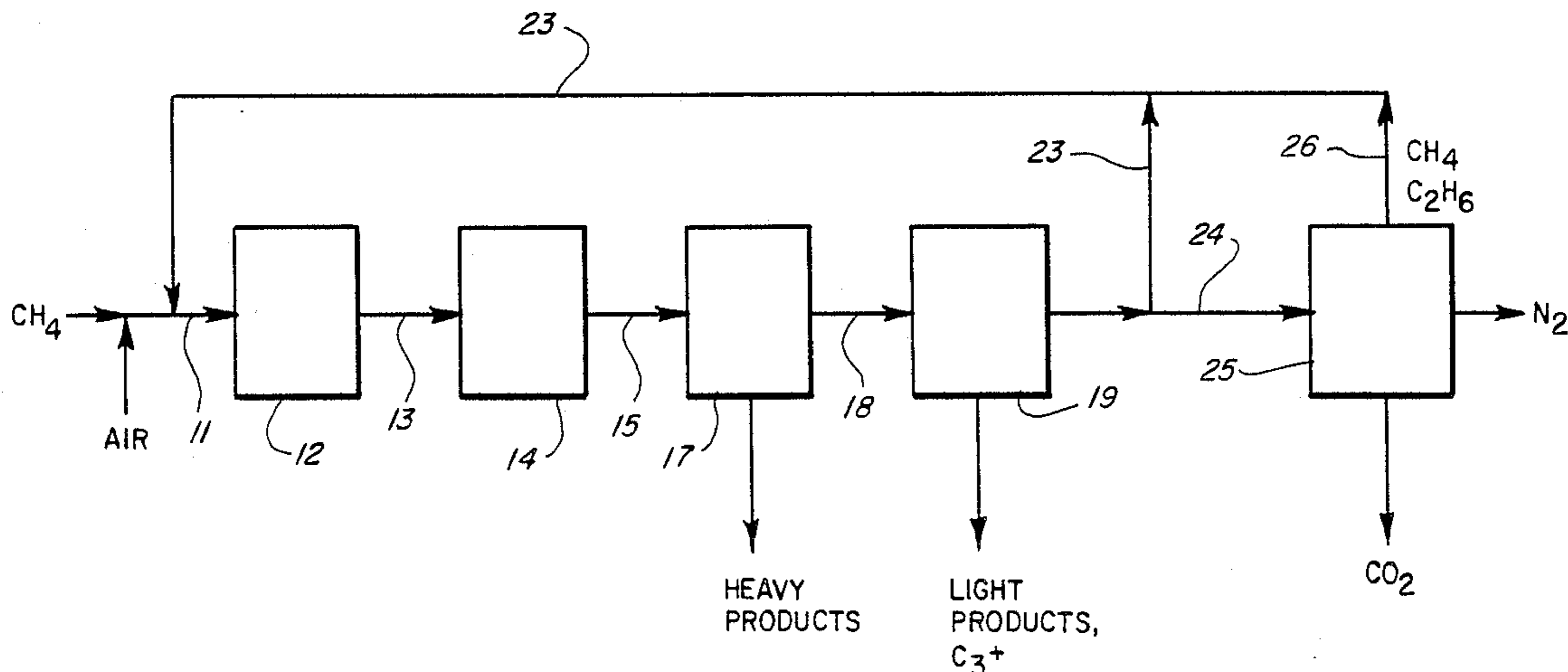
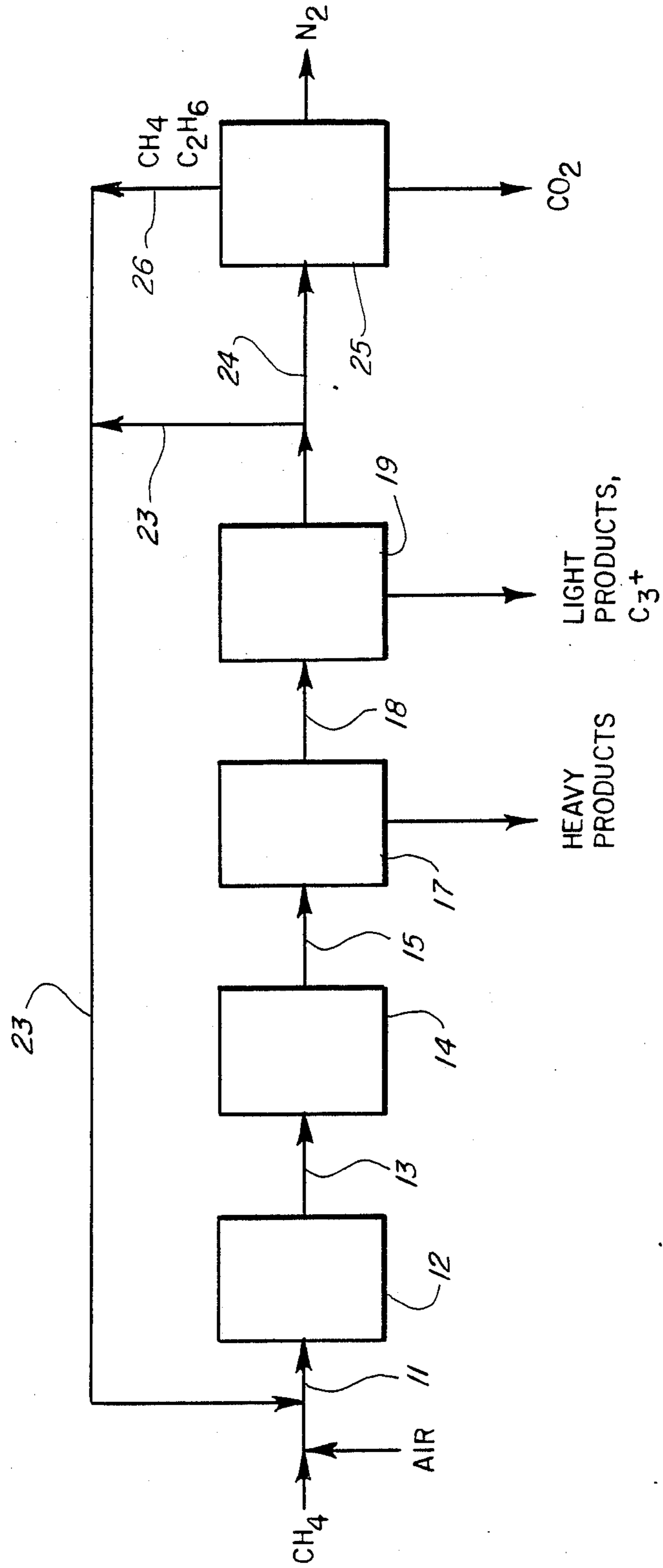


FIG. 1



## CONVERSION OF A LOWER ALKANE

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

This invention relates generally to the conversion of a lower molecular weight alkane to more valuable, heavier hydrocarbons, and more particularly concerns an aforesaid process which comprises the oxidative coupling of the alkane.

#### 2. Description of the Prior Art

A major source of lower molecular weight alkanes is natural gas. Lower molecular weight alkanes are also present in coal deposits and are formed during numerous mining operations, in various petroleum processes and in the above- or below-ground gasification or liquefaction of coal, tar sands, oil shale and biomass.

It is highly desirable to convert lower molecular weight alkanes to more valuable and higher molecular weight materials and a number of attempts to do so have been reported. For example, G. E. Keller and M. M. Bhasin (J. Catal. 73, 1982, 9-19) have shown that in the presence of catalysts methane can be converted to C<sub>2</sub> hydrocarbons, but that the yields of ethylene and ethane are low and amount to only from 10 to 50 percent of the reacted methane. To improve the selectivity for the production of the desired C<sub>2</sub> hydrocarbons and to suppress the undesirable further reaction of the C<sub>2</sub> hydrocarbons initially formed to produce carbon dioxides, Keller and Bhasin propose a special reaction method: the catalyst is first charged with oxygen by the passage over it of a gas containing oxygen; then in a second step, the oxygen in the gas chamber of the catalytic reactor is replaced by an inert gas; in a third step, methane is fed over the catalyst which partially produces the desired reaction; in a fourth and last step, an inert gas is again led through the reactor to supplant the residual methane and the resulting product, before the sequence of steps is repeated. In this process, depending on the catalyst used and the temperature selected, the selectivities for the production of C<sub>2</sub> hydrocarbons range from about 5 to about 45%, and the selectivities for the production of CO<sub>2</sub> range from about 55 to 95%, with the conversions of methane ranging between 1 and 10%.

Keller and Bhasin arrives at the conclusion that the oxidative coupling is only highly selective to the higher hydrocarbons when the reaction takes place in the absence of gas-phase oxygen and the oxidative coupling of the hydrocarbons should be caused by reaction with the lattice oxygen of the metal oxides, which are thus reduced by two valency stages. Since the lattice oxygen available in the catalyst is predetermined, for every measured unit of the catalyst only a limited quantity of hydrocarbons can be reacted.

It is evident that the modus operandi in Keller and Bhasin is costly in terms of apparatus as well as being simultaneously linked with small yields in space-time terms and high operating and investment costs. Moreover, the attainable methane conversions and/or the resultant space-time yields are too small for a commercial installation according to the data of the authors. Furthermore, the only products reported are C<sub>2</sub> hydrocarbons.

Jones et al., U.S. Pat. Nos. 4,443,664-9 disclose methods for synthesizing hydrocarbons containing as many as 7 carbon atoms from a methane source which comprise contacting methane with a reducible oxide of antimony, germanium, bismuth, lead, indium or manganese.

These patents also disclose that the reducible oxides can be supported by a conventional support material such as silica, alumina, titania, and zirconia. Specific supports disclosed are Houdry HSC 534 silica, Cab-O-Sil, Norton alpha-alumina and Davison gamma-alumina. The ranges of reaction temperatures disclosed in the aforesaid patents are from a lower limit of 500° C. to an upper limit of 800° C.-1000° C. In the disclosed processes, the reducible oxide is first reduced and is then regenerated by oxidizing the reduced composition with molecular oxygen, either in a second zone or by alternating the flow of a first gas comprising methane and the flow of an oxygen-containing gas. The highest yield of hydrocarbon products reported was only about 2.1% of the methane feed, when a reducible oxide of manganese was employed.

Furthermore, Baerns, West German Patent Application No. 3,237,079.2, discloses a method for the production of ethane or ethylene by the reaction of methane and an oxygen-containing gas at a temperature between 500° C. and 900° C., at an oxygen partial pressure of less than about 0.5 atmosphere at the reactor entrance, with a ratio of methane partial pressure-to-oxygen partial pressure greater than 1 at the reactor entrance and in the presence of a solid catalyst free of acidic properties. As disclosed, the method can be performed with or without recycle of remaining unreacted methane. The highest molecular weight product formed in the disclosed method is propane, and the highest collective selectivity for the formation of ethane, ethylene and propane is only about 65% of the methane converted.

Baerns discloses that oxides of the metals of Groups III-VII of the Periodic Table are suitable for use as catalysts in the method disclosed therein and that the oxides of lead, manganese, antimony, tin, bismuth, thallium, cadmium and indium are particularly preferred. Baerns further discloses that the metal oxides can be employed with or without a carrier and that specifically preferred carriers are alumina, silica, silicon carbide and titania. Specific examples of carrier materials disclosed were formed from gamma-alumina having BET surface areas of 160-166 m<sup>2</sup>/gm, silica having a BET surface area of 290 m<sup>2</sup>/gm, bismuth oxide, aluminum silicate, and titania.

### OBJECTS OF THE INVENTION

It is therefore a general object of the present invention to provide a method for converting a lower molecular weight alkane to more valuable, higher molecular weight, heavier hydrocarbons which meets the aforementioned requirements and solves the aforementioned problems of prior art methods.

More particularly, it is an object of the present invention to provide a method for converting a lower molecular weight alkane to more valuable, higher molecular weight hydrocarbons with a high degree of conversion of the alkane.

It is another object of the present invention to provide a method for converting a lower molecular weight alkane to more valuable, higher molecular weight hydrocarbons with a high degree of selectivity for the production of liquid hydrocarbons.

It is a similar object of the present invention to provide a method for converting a lower molecular weight alkane to more valuable, higher molecular weight hydrocarbons which affords a high yield of liquid hydrocarbons.

Other objects and advantages of the present invention will become apparent upon reading the following detailed description and appended claims, and upon reference to the accompanying drawing.

### SUMMARY OF THE INVENTION

These objects are achieved by an improved method for converting at least one feedstock alkane containing from 1 to 3 carbon atoms to more valuable, higher molecular weight hydrocarbons, comprising: (a) contacting the feedstock alkane containing from 1 to 3 carbon atoms with an oxygen-containing gas in a reactor in the presence of an oxidative coupling catalyst at a temperature in the range of from about 600° C. to about 1000° C., to thereby produce a gaseous mixture comprising any remaining unreacted feedstock alkane and oxygen and saturated and unsaturated aliphatic hydrocarbon products having higher molecular weights than the feedstock alkane from which they were formed; and (b) contacting the resulting gaseous mixture with an oligomerization catalyst under aromatization conditions to thereby produce a gaseous mixture comprising any remaining unreacted feedstock alkane and oxygen and an aromatic product and a saturated aliphatic hydrocarbon product having a higher molecular weight than the feedstock alkane from which it was produced.

### BRIEF DESCRIPTION OF THE DRAWING

For a more complete understanding of this invention, reference should now be made to the embodiments illustrated in greater detail in the attached drawing and described below by way of examples of the invention. In the drawing, FIG. 1 is a schematic illustration of a preferred embodiment of the present invention in which: (a) a methane feedstock is combined with air in the presence of an oxidative coupling catalyst and is initially partially converted to a mixture comprising ethane and ethylene; (b) the ethylene in the resulting product stream is catalytically aromatized; (c) the resulting heavy aromatic product is separated from the product mixture; (d) the resulting light aromatic product is separated from the product mixture; (e) after separation of a slip stream from the remaining product mixture, the remaining product mixture is recycled to step (a) for additional conversion of remaining unreacted feedstock alkane; and (f) at least a portion of the methane component of the slip stream is separated from the slip stream and recycled to step (a) for additional conversion of remaining unreacted feedstock alkane.

It should be understood that the drawing is a schematic illustration, and that in certain instances, details which are not necessary for an understanding of the present invention or which render other details difficult to perceive may have been omitted. It should be understood, of course, that the invention is not necessarily limited to the particular embodiments illustrated herein.

### DETAILED DESCRIPTION OF THE DRAWING INCLUDING PREFERRED EMBODIMENTS

Turning first to FIG. 1, there is shown schematically a preferred embodiment of the method of this invention. Methane, illustrative of a feedstock comprising at least one alkane containing from 1 to 3 carbon atoms is mixed with air, as a source of oxygen, and the resulting mixture is introduced through line 11 into a first reactor 12 where it is contacted with a suitable catalyst for the oxidative coupling of the aforesaid alkane. The effluent from the first reactor 12 is a gaseous product stream

comprising carbon dioxide, nitrogen, any remaining unreacted feedstock alkane and oxygen, and ethane and ethylene, illustrative of alkane and alkene products having higher molecular weights than the feedstock alkane from which they were formed, and is introduced through line 13 into a second reactor 14, where it is contacted with a suitable oligomerization catalyst under aromatization conditions. The effluent from the second reactor 14 comprises carbon dioxide, nitrogen, any remaining unreacted feedstock alkane and oxygen, and higher molecular weight alkane and aromatic products, and is passed through line 15 and a first separator 17 where the separation of any higher boiling products produced in the second reactor 14 is effected. The remaining lower boiling materials are then withdrawn as a gaseous mixture in line 18 from the first separator 17 and introduced into a second separator 19 where lower boiling, normally liquid products and optionally at least a portion of the gaseous hydrocarbon products having molecular weights above the feedstock alkane are separated. The gaseous effluent from the second separator 19, comprising carbon dioxide, nitrogen and any remaining unreacted feedstock alkane and oxygen, is then split into two streams. The first resulting stream is a major portion of the gaseous effluent from the second separator 19, and is recycled in line 23 as feedstock back to the first reactor 12. The second resulting stream is a minor portion of the gaseous effluent from the second separator 19, has the same composition as the aforesaid first resulting stream, but is passed in line 24 through a third separator 25 where at least a portion of its methane and ethane components is removed therefrom and recycled through line 26 and line 23 as feedstock back to the first reactor 12.

It should be understood that FIG. 1 illustrates merely one preferred embodiment of the method of this invention and that the present invention is not limited to the particular embodiment illustrated in FIG. 1.

Generally, a suitable feedstock for the method of this invention comprises at least one of methane, ethane and propane, preferably comprises methane and more preferably comprises a mixture of methane and ethane. Thus, a suitable feedstock for the method of this invention comprises natural gas, gases formed during mining operations, in petroleum processes or in the above- or below-ground gasification or liquefaction of coal, tar sands, oil shale and biomass.

The oxygen-containing gas for use in the method of this invention can vary in molecular oxygen content from that of air to oxygen gas itself. Air or enriched air is a preferred source of molecular oxygen. The oxygen-containing gas should provide a gas-vapor effluent mixture from the oxidative coupling reactor containing (measured on a solid-free basis) from about 2 to about 8 volume percent of oxygen, in order to avoid the flammability limits in such mixture.

The oxidative coupling reaction is performed at a temperature in the range of from about 600° C. to about 1000° C., preferably in the range of from about 700° C. to about 850° C. The oxidative coupling step of the method of this invention is performed under a total absolute pressure preferably in the range of from about 1 atmosphere to about 10 atmospheres, and more preferably in the range of from about 1 atmosphere to about 5 atmospheres. The ratio of the combined partial pressures of the feedstock alkanes containing from 1 to 3 carbon atoms in the feedstock-to-the oxygen partial pressure at the entrance of the reactor in the oxidative

coupling step is preferably in the range of from about 2:1 to about 40:1 and more preferably in the range of from about 5:1 to about 30:1. The combined partial pressures of the alkanes in the feedstock containing from 1 to 3 carbon atoms at the entrance to the oxidative coupling reactor is preferably in the range of from about 0.1 to about 10 atmospheres, and more preferably in the range from about 0.2 to about 5 atmospheres. The oxygen partial pressure at the entrance to the oxidative coupling reactor is preferably in the range from about 0.01 to about 5 atmospheres and more preferably in the range of from about 0.02 to about 0.7 atmospheres. The oxygen partial pressure in the gaseous effluent from the reactor in the oxidative coupling step is preferably substantially zero.

The oxidative coupling step is performed preferably at a space velocity, calculated for a reaction pressure of one atmosphere absolute, of from about 100 to about 10,000 cubic centimeters of total feed gas comprising feedstock alkane containing from 1 to 3 carbon atoms per hour per cubic centimeter of catalyst and more preferably at a space velocity of from about 500 to about 5000 cubic centimeters of total feed gas comprising feedstock alkane containing from 1 to 3 carbon atoms per hour per cubic centimeter of catalyst. For the purposes of this definition of the space velocity, the feedstock alkane comprises from about 10 volume percent to about 80 volume percent of the total feed gas.

In one embodiment, the catalyst employed in the oxidative coupling step of the method of this invention comprises silica having a surface area less than about 175 m<sup>2</sup>/gm. Preferably, the silica has a surface area of from about 5 m<sup>2</sup>/gm to about 75 m<sup>2</sup>/gm. More preferably, the catalyst is silica. It is also preferred that the silica is calcined at a temperature of from about 800° C. to about 1100° C. for from about 2 hours to about 36 hours. More preferably, the silica is calcined at a temperature of from about 950° C. to about 1050° C. for from about 4 hours to about 16 hours.

In another embodiment, the catalyst employed in the oxidative coupling step of the method of this invention comprises a reducible compound of lead, antimony, germanium, vanadium, tin, bismuth, cadmium, indium, manganese, thallium, or a mixture thereof. Preferably, the reducible compound employed is an oxide, sulfide, sulfate, or carbonate of lead, antimony, germanium, vanadium, tin, bismuth, cadmium, indium, manganese, thallium, or a mixture thereof. The oxidative coupling catalyst more preferably comprises a reducible compound of lead and most preferably comprises a lead oxide. If a reducible compound of lead is present, the presence of additional reducible compounds of other metals, such as zirconium and titanium, which themselves are not effective catalysts, serves to promote the activity of the lead compound in the oxidative coupling reaction.

Preferably, the oxidative coupling catalyst employed in the method of this invention comprises, in addition to the aforesaid reducible metal compound, an amorphous refractory inorganic oxide support comprising an oxide of an element from Groups IIA, IIIA, IIIB, IVA or IVB of the Periodic Table. More preferably, the amorphous refractory inorganic oxide support of the oxidative coupling catalyst employed in the method of this invention comprises silica, alumina, silica-alumina, silica-stabilized alumina, phosphated alumina, silica-stabilized phosphated alumina, alumina-aluminum phosphate, borialumina, magnesia-alumina, boria, magne-

sia, or titania. Such amorphous refractory inorganic oxide support preferably comprises silica having a surface area in the range of from about 1 m<sup>2</sup>/gm to about 175 m<sup>2</sup>/gm, and more preferably in the range of from about 5 m<sup>2</sup>/gm to about 75 m<sup>2</sup>/gm. The amorphous refractory inorganic oxide support of the oxidative coupling catalyst employed in the method of this invention more preferably is silica.

The reducible compound component of the oxidative coupling catalyst employed in the method of this invention comprises preferably from about 2 weight percent to about 50 weight percent of the oxidative coupling catalyst, and more preferably from about 10 weight percent to about 30 weight percent of the oxidative coupling catalyst, calculated as the oxide of the reducible metal and based on the total weight of the oxidative coupling catalyst.

The oxidative coupling catalyst preferably employed in the method of this invention can be prepared by impregnation of the aforesaid amorphous refractory inorganic oxide support with at least one precursor of the reducible metal compound. Any convenient, conventional impregnation technique can be employed for this purpose. For example, a soluble compound of the metal of the reducible metal oxide can be added to a sol or gel of the amorphous refractory inorganic oxide. This composition is then thoroughly blended into the sol or gel mixture, and subsequently co-gelled by the addition of a dilute ammonia solution. The resulting co-gelled material is then dried. In another method of preparation, the refractory inorganic oxide is gelled, dried, and cooled and the resulting material is then impregnated with one or more solutions of a soluble compound of the metal of the reducible metal oxide. Preferably, as will be described hereinbelow, the support containing the reducible metal compound or precursor thereof is calcined, regardless of the method of preparation used. In such case, the calcination conditions are preferably at a temperature of from about 500° C. to about 1050° C. for from about 2 hours to about 36 hours and more preferably calcination in air at a temperature of from about 950° C. to about 1050° C. for from about 4 hours to about 20 hours. More preferably, the support is also calcined prior to incorporating the reducible metal compound or its precursor therein, and in such cases the calcination conditions employed are as described hereinabove for the calcination of silica.

It has been found that the selectivity of the oxidative coupling catalyst for the formation of coupled products can be increased by the additional incorporation therein of an alkali metal component into the support. The presence of the alkali metal component in the oxidative coupling catalyst also permits the concentration of the reducible metal component in the catalyst to be reduced without decreasing the selectivity of the catalyst for the formation of coupled products. Preferably, the metal of the alkali metal component is sodium, potassium or lithium. The alkali metal component is present in the catalyst at a concentration of preferably from about 0.1 to about 6 weight percent, more preferably from about 0.5 to about 3 weight percent, calculated as the alkali metal oxide and based on the weight of the catalyst. A compound of the alkali metal can be deposited by any convenient, conventional technique such as impregnation or spray drying, before, during or after deposition of the metal of the reducible metal component on the catalyst support. Upon calcination, the alkali metal component is converted to the form of its metal oxide.

The gaseous mixture resulting from the oxidative coupling reaction comprises any remaining unreacted feedstock alkane and oxygen and saturated and unsaturated aliphatic hydrocarbon products having higher molecular weights than the feedstock alkane from which they were formed. In addition, if air is employed as the source of molecular oxygen in the oxidative coupling step of the method of the present invention, the effluent from the oxidative coupling step also contains nitrogen and carbon dioxide.

In order to increase the conversion of the feedstock alkane in the oxidative coupling step and the yield of the desired products therefrom, it is desirable to recycle the unconverted feedstock alkane to the oxidative coupling step in a preferred embodiment of the method of this invention. However, recycle of the entire gaseous product mixture from the oxidative coupling reaction to the oxidative coupling step results in a decrease of both the selectivity for the formation of coupled products and the yield of coupled products. Although the presence of saturated coupled products such as ethane in the feed to the oxidative coupling reaction and, hence, in the product mixture recycled to the oxidative coupling reaction, affords a surprising increase in the selectivity for both the formation of coupled products and the yield of coupled products in the oxidative coupling step, the presence of unsaturated coupled products such as ethylene and acetylene in the feed to the oxidative coupling reaction and, hence, in the recycled product mixture had a substantial deleterious effect on the selectivity for the formation of and yield of coupled products in the oxidative coupling step. Thus, in order to increase the conversion of the feedstock alkane and yield of the desired products therefrom, the recycled gaseous mixture must be relatively free of unsaturated coupled products.

Thus, in a preferred embodiment of the method of this invention, prior to being recycled, the gaseous product mixture from the oxidative coupling reaction is contacted with an oligomerization catalyst under aromatization conditions in order to remove unsaturated coupled products therefrom. Surprisingly, the use of certain acidic oligomerization catalysts permits substantially complete removal of the unsaturated hydrocarbons even at atmospheric pressure and from the dilute hydrocarbon streams from the oxidative coupling reaction. The aromatization conditions include a temperature preferably in the range of from about 50° C. to about 500° C. and more preferably in the range of from about 200° C. to about 400° C. The aromatization conditions also include a total absolute pressure preferably in the range of from about 1 atmosphere to about 10 atmospheres and more preferably in the range of from about 1 atmosphere to about 5 atmospheres. The aromatization conditions also include a space velocity, calculated for a reaction pressure of one atmosphere absolute, preferably in the range of from about 100 to about 5,000 cubic centimeters of the gaseous mixture per hour per cubic centimeter of the oligomerization catalyst and more preferably in the range of from about 200 to about 2,000 cubic centimeters of the gaseous mixture per hour per cubic centimeter of the oligomerization catalyst.

The oligomerization catalyst comprises a solid having acidic sites and comprising a molecular sieve, a pillared smectite or vermiculite clay or a combination thereof, or a combination thereof with an amorphous refractory inorganic oxide. Suitable molecular sieves for use in the oligomerization catalyst employed in the method of this

invention include a crystalline aluminosilicate, crystalline borosilicate, or de-aluminated crystalline aluminosilicate, or combination thereof. A suitable crystalline aluminosilicate includes natural or synthetic chabazite, clinoptilolite, erionite, mordenite, zeolite A, zeolite L, zeolite X, zeolite Y, ultrastable zeolite Y, zeolite omega, or a ZSM-type zeolite such as ZSM-5, ZSM-11, ZSM-12, ZSM-35, ZSM-38 or ZSM-48.

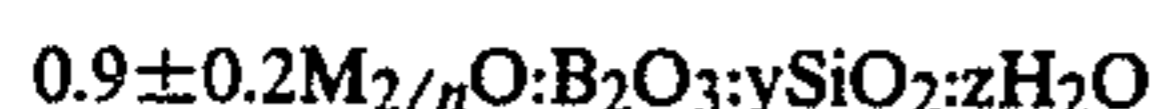
Mordenite-type crystalline aluminosilicates have been discussed in the patent art, for example, in Kimberlin, U.S. Pat. No. 3,247,098; Benesi et al., U.S. Pat. No. 3,281,483; and Adams et al., U.S. Pat. No. 3,299,153. Synthetic mordenite-type crystalline aluminosilicates, designated as Zeolon, are available from the Norton Company of Worcester, Mass. Another example of a crystalline molecular sieve that is suitable for use in the oligomerization catalyst employed in the method of the present invention is a Y-type zeolitic crystalline aluminosilicate. Y-type, zeolitic molecular sieves are discussed in U.S. Pat. No. 3,130,007.

Ultrastable, large-pore, Y-type, zeolitic crystalline aluminosilicate material is also suitable for use in the oligomerization catalyst in the method of this invention and is described in U.S. Pat. Nos. 3,293,192 and 3,449,070. By large-pore material is meant a material that has pores which are sufficiently large to permit the passage therinto of benzene molecules and larger molecules and the passage therefrom of reaction products. The ultrastable, large-pore, Y-type, zeolitic crystalline aluminosilicate material that is suitable for use in the oligomerization catalyst employed in the method of this invention exhibits a cubic unit cell dimension and hydroxyl infrared bands that distinguish it from other aluminosilicate materials. The cubic unit cell dimension of the aforesaid ultrastable, large-pore, crystalline aluminosilicate is within the range of about 24.20 Å to about 24.55 Å. The hydroxyl infrared bands obtained with the aforesaid ultrastable, large-pore, crystalline aluminosilicate material are a band near 3,745 cm<sup>-1</sup> (3,745 ± 5 cm<sup>-1</sup>), a band near 3,695 cm<sup>-1</sup> (3,690 ± 10 cm<sup>-1</sup>), and a band near 3,625 cm<sup>-1</sup> (3,610 ± 15 cm<sup>-1</sup>). The band near 3,745 cm<sup>-1</sup> may be found on many of the hydrogen-form and de-cationized aluminosilicate materials, but the band near 3,695 cm<sup>-1</sup> and the band near 3,625 cm<sup>-1</sup> are characteristic of the aforesaid ultrastable, large-pore, Y-type, zeolitic crystalline aluminosilicate material that is used in the catalyst of the present invention. The ultrastable, large-pore, Y-type, zeolitic crystalline aluminosilicate material is also characterized by an alkaline metal content of less than 1%.

Other molecular sieve materials that are useful in the catalyst employed in the method of the present invention are ZSM-type crystalline aluminosilicate molecular sieves. Suitable crystalline aluminosilicates of this type typically have silica-to-alumina mole ratios of at least about 12:1 and pore diameters of at least 5 Å. A specific example of a useful crystalline aluminosilicate zeolite of the ZSM-type is ZSM-5, which is described in detail in U.S. Pat. No. 3,702,886. Other crystalline aluminosilicate zeolites of the ZSM-type contemplated according to the invention include ZSM-11, which is described in detail in U.S. Pat. No. 3,709,979; ZSM-12, which is described in detail in U.S. Pat. No. 3,832,449; ZSM-35, which is described in U.S. Pat. No. 4,016,245; and ZSM-38, which is described in detail in U.S. Pat. No. 4,046,859. A preferred crystalline aluminosilicate zeolite of the ZSM-type is ZSM-5.

Dealuminated crystalline aluminosilicate zeolites having higher silica-to-alumina mole ratios than in those formed by available synthesis of crystalline aluminosilicate zeolites are also suitable for use in the oligomerization catalyst of the method of the present invention and can be produced by the removal of aluminum from the structural framework of the crystalline aluminosilicate zeolite by appropriate chemical agents. A considerable amount of work on the preparation of aluminum deficient faujasites has been performed and is reviewed in *Advances in Chemistry, Series No. 121, "Molecular Sieves,"* G. T. Kerr, American Chemical Society, 1973. Specific methods for preparing dealuminized zeolites are described in the following, and reference is made to them for details of the method: *Catalysis by Zeolites* (International Symposium on Zeolites, Lyon, Sept. 9-11, 1980), Elsevier Scientific Publishing Co., Amsterdam, 1980 (dealuminization of zeolite Y with silicon tetrachloride); U.S. Pat. No. 3,442,795 and British Pat. No. 1,058,188 (hydrolysis and removal of aluminum by chelation); British Pat. No. 1,061,847 (acid extraction of aluminum); U.S. Pat. No. 3,493,519 (aluminum removal by steaming and chelation); U.S. Pat. No. 3,591,488 (aluminum removal by steaming); U.S. Pat. No. 4,273,753 (dealuminization by silicon halides and oxyhalides); U.S. Pat. No. 3,691,099 (aluminum extraction with acid); U.S. Pat. No. 4,093,560 (dealuminization by treatment with salts); U.S. Pat. No. 3,937,791 (aluminum removal with Cr(III) solutions); U.S. Pat. No. 3,506,400 (steaming followed by chelation); U.S. Pat. No. 3,640,681 (extraction of aluminum with acetylacetonate followed by dehydroxylation); U.S. Pat. No. 3,836,561 (removal of aluminum with acid); DE-OS No. 2,510,740 (treatment of zeolite with chlorine or chlorine-contrary gases at high temperatures), Dutch Pat. No. 7,604,264 (acid extraction), Japanese No. 53,101,003 (treatment with EDTA or other materials to remove aluminum) and *J. Catalysis*, 54, 295 (1978) (hydrothermal treatment followed by acid extraction).

An additional molecular sieve that can be used in the oligomerization catalyst of the present invention is a crystalline borosilicate, which is described in Klotz, U.S. Pat. No. 4,269,813, which patent is specifically incorporated herein by reference. A suitable crystalline borosilicate is a molecular sieve material having the following composition in terms of mole ratios of oxides:



wherein M is at least one cation having a valence of n, y is within the range of 4 to about 600, and z is within the range of 0 to about 160, and providing an X-ray pattern providing the following X-ray diffraction lines and assigned strengths:

d, Angstroms	Assigned Strength
11.2 ± 0.2	W-VS
10.0 ± 0.2	W-MS
5.97 ± 0.07	W-M
3.82 ± 0.05	VS
3.70 ± 0.05	MS
3.62 ± 0.05	M-MS
2.97 ± 0.02	W-M
1.99 ± 0.02	VW-M

Suitable methods for preparing the aforesaid crystalline borosilicate molecular sieve are disclosed in Klotz, U.S. Pat. No. 4,269,813 and in Haddid, European Patent

Application No. 82303246.1 which was published on Jan. 5, 1983.

Pillared smectite and vermiculite clays, which are also suitable for use in, or as, the oligomerization catalyst employed in the method of this invention, are often referred to in the literature as pillared interlayered clays and occasionally as molecular sieves. The smectite clays comprise montmorillonite, beidellite, montronite, volchonskoite, hectorite, saponite, stevensite, sauconite and pimelite. Some pillared smectite and vermiculite clay materials that are suitable for use in the support of the catalyst employed in the method of this invention, and methods for preparing such clays, are disclosed in Vaughan et al., U.S. Pat. No. 4,176,090; Shabria et al., U.S. Pat. No. 4,216,188; Shabtai, U.S. Pat. No. 4,238,364; D'Aniello, U.S. Pat. No. 4,380,510; Pinnavaia, "Intercalated Clay Catalysts," *Science*, Vol. 220, pages 365-371 (Apr. 22, 1983) and Vaughan et al., "Preparation of Molecular Sieves Based on Pillared Interlayered Clays (PILC)," *Fifth International Conference on Zeolites*, pages 94-101 and in the references cited therein. Preferably, a suitable pillared smectite or vermiculite clay comprises a multiplicity of cations interposed between the molecular layers of the clay and maintaining the spacing between the molecular layers in the range of from about 6 Å to about 10 Å at a temperature of at least 300° C. in an air atmosphere for at least 2 hours.

Preferably, when the oligomerization catalyst comprises an aforesaid molecular sieve material or an aforesaid pillared smectite or vermiculite clay material or a combination thereof, the oligomerization catalyst also comprises a porous amorphous refractory inorganic oxide comprising an oxide of an element from Groups IIA, IIIA, IIIB, IVA or IVB of the Periodic Table. In such cases, the concentrations of the amorphous inorganic oxide and of the molecular sieve material and/or pillared smectite or vermiculite clay material are not critical. Preferably, the amorphous refractory inorganic oxide content is at least high enough to give the oligomerization catalyst sufficient strength and integrity so that it can be employed in the method of the present invention without appreciable damage to the catalyst. In such case, the total concentration of the molecular sieve material and/or pillared smectite or vermiculite clay material in such mixture is preferably from about 5 to about 95 weight percent, and the total concentration of the amorphous refractory inorganic oxide in the mixture is preferably from about 5 to about 95 weight percent, based on the weight of the support.

Preferably, when the oligomerization catalyst comprises a mixture of a molecular sieve and/or pillared smectite or vermiculite clay and an amorphous refractory inorganic oxide, the oligomerization catalyst is in the form of a dispersion of the molecular sieve component and/or pillared smectite or vermiculite clay component in a matrix of the amorphous refractory inorganic oxide. Such dispersions can be prepared by well-known techniques, such as blending the molecular sieve component and/or pillared smectite or vermiculite clay component, preferably in finely-divided form, into a sol, hydrosol or hydrogel of the amorphous refractory inorganic oxide, and then adding a gelling medium, such as ammonium hydroxide, and stirring to produce a gel. Alternately, the molecular sieve component and/or pillared smectite or vermiculite clay component is blended into a slurry of the amorphous inorganic oxide. In either case, the resulting mixture can be dried,

shaped, if desired, and then calcined to form the final support component. A less preferred, but still suitable, method for preparing a suitable dispersion of the molecular sieve component and/or pillared smectite or vermiculite clay component in the amorphous refractory inorganic oxide is to dry-blend particles of each, preferably in finely-divided form, and then to conduct any desired shaping operations, such as pelletizing or extrusion; the resulting mixture is then calcined.

The oligomerization catalyst employed in the method of this invention comprises a solid having acidic sites. Consequently, it is highly preferred that the aforesaid molecular sieve or pillared clay materials containing exchangeable cations and employed in the oligomerization catalyst are in their proton-exchanged forms. The proton forms of these materials are particularly effective at the low pressures employed in the oligomerization step of the method of this invention.

The aforesaid molecular sieve and pillared clay materials could also be in their metal-exchanged or metal-impregnated forms, provided that such metal-containing materials still have acidic properties. In such case, the metal employed should be one, such as zinc, which promotes the oligomerization-aromatization activity of the catalyst. Any convenient, conventional cation-exchange or cation-impregnation technique can be employed for this purpose.

Suitable conditions for drying the above-described supports comprise a temperature in the range of from about 90° C. to about 200° C. and a drying time of from about 0.5 to about 30 hours. Suitable calcination conditions in such methods comprise a temperature in the range of about 480° C. to about 760° C. and a calcination time of from about 2 to about 5 hours. Preferred drying and calcination conditions are a temperature of about 120° C. for about 1-2 hours and a temperature of about 538° C. for about 1-2 hours, respectively.

The gaseous mixture resulting from the oligomerization reaction comprises any remaining unreacted feedstock alkane and oxygen and a heavy aromatics product, a light aromatics product and at least one higher molecular weight saturated aliphatic hydrocarbon product. Prior to recycling the unreacted feedstock alkane component of this mixture to the oxidative coupling step, the desired hydrocarbon products are separated from it. This can be effected using any convenient, conventional method. One suitable method to accomplish this separation involves first separating the higher boiling, liquefiable products such as alkylbenzenes and alkylnaphthalenes by scrubbing the gaseous mixture in a suitable solvent as a sufficiently low temperature, such as a cooled oil scrubber, such that the aforesaid liquefiable products are selectively dissolved in it. The resulting liquefied products are recovered from the oil scrubber, for example, by distillation of the scrubbing oil. The remaining gaseous components of the product stream comprise remaining unreacted feedstock alkane and oxygen and lower boiling products such as lighter aromatics and saturated aliphatics and pass through the oil scrubber as a gaseous mixture.

The lower boiling products are next separated from this mixture by any convenient, conventional technique. One highly effective, novel technique involves passing the mixture through a charcoal bed. The unreacted feedstock alkane and oxygen pass through the charcoal bed faster than do the products and are recycled to the oxidative coupling step before the products saturate and emerge from the bed. When the bed becomes saturated

with the products, the products begin to emerge from the bed, and the bed is removed from service and replaced in service by a fresh charcoal bed. The lower boiling products are then removed from the saturated bed and collected. This separation step can be performed either by removing the bed from service when the lowest boiling product, for example, ethane, begins to emerge from the bed or, as illustrated in FIG. 1, by removing the bed from service when higher boiling (but still low boiling) products, for example, C<sub>3</sub>+ hydrocarbons, begin to emerge from the bed.

The adsorption or saturation step is conducted at a lower temperature than the desorption or product-removal step. The gases enter the charcoal bed at a temperature, for example, below about 65° C. and at substantially atmospheric pressure absolute. Under these conditions as much as 20-30 percent of the weight of the bed is covered by adsorbed product. When the bed can hold no more hydrocarbon as shown by the presence of higher hydrocarbons in the effluent gas from the charcoal bed, the feed gas is stopped and superheated steam is passed into the bed. As the bed heats up, it desorbs hydrocarbons which pass out of the bed with excess steam and are condensed out in a separate operation. When the bed has been heated to some temperature preferably in the range of 105°-300° C. and desorption of hydrocarbons has diminished substantially, the charcoal bed is cooled down and then returned to service. Any oleophilic charcoal works well, as do certain hydrophobic clays. In particular, coconut and bituminous charcoal have been shown to be both highly effective and inexpensive.

When the oxygen-containing gas comprises air, the gaseous mixture which remains after the step of recovering the lower boiling products comprises nitrogen and carbon dioxide in addition to remaining unreacted feedstock alkane and oxygen. Thus, nitrogen and carbon dioxide would build up in the recycled portion of the feed to the oxidative coupling step. This buildup of nitrogen and carbon dioxide in the recycle to the oxidative step can be eliminated conveniently by separating a slip stream from the recycle gas and venting a small portion, for example, 10 percent, of the recycle gas before the recycle gas is returned to the oxidative coupling step. However, in addition to nitrogen and carbon dioxide, the gas vented also contains some unreacted feedstock alkane. In order to maximize the conversion of the feedstock alkane to coupled products, it is desirable to separate the unreacted feedstock alkane component from the slip stream before it is vented and recycle the separated feedstock alkane to the oxidative coupling step. This separation can be effected by any convenient, conventional technique. One highly effective, novel technique involves passing the slip stream through a second charcoal bed. The nitrogen passes through the charcoal bed faster than does the unreacted feedstock alkane and is vented before the unreacted feedstock alkane saturates and emerges from the bed. When the bed becomes saturated with feedstock alkane, the feedstock alkane begins to emerge from the bed, the bed is removed from service and replaced in service by a fresh charcoal bed. The feedstock alkane is then removed from the saturated bed and recycled to the oxidative coupling step.

For reclaiming feedstock alkane from the slip stream, a somewhat different mode of operating the charcoal bed is more advantageous than that described hereinabove. In this case, because of the low adsorptive ca-



capacity that charcoals have for methane, it is desirable to use rapid adsorption-desorption cycles, without externally changing the temperature of the bed. It has been advantageous when such beds become saturated with methane, ethane and carbon dioxide (the nitrogen having been discharged) at a temperature up to 65° C. and at substantially atmospheric pressure absolute, to remove adsorbed methane by evacuating the bed. With progressive evacuation down to about 28–29 inches of mercury vacuum, methane, carbon dioxide, and ethane are removed separately and sequentially, thus permitting an effective separation of such components. Methane and, if desired, higher hydrocarbons are returned to the recycle system; while carbon dioxide is selectively rejected.

In an alternative embodiment, the higher hydrocarbon products are converted to unsaturated materials, for example, by thermal cracking or oxidative dehydrogenation, to form unsaturated hydrocarbons which can then be recycled to step (b) for aromatization.

The present invention will be more clearly understood from the following specific examples.

#### EXAMPLES 1–149

Examples 1–149 demonstrate significant parameters of the oxidative coupling reaction of the method of this invention. In each of Examples 1–149, a stream of methane and air was passed through a heated quartz tube (except Examples 28–31 where a ceramic reactor was used) having an inside diameter of 1.43 centimeters and a length of from 10 to 43 centimeters and, in all cases except Examples 1–4 and 28–31, whose internal volume in the middle of the tube was filled with solid particles or pellets. The reaction pressure was approximately one atmosphere absolute. The product gas effluent from the tube was cooled with an ice bath condenser and analyzed. The experimental parameters employed in Examples 1–149 and the results therefrom are presented in Tables 1–19. In all cases except Examples 1–4 and 28–31, the units of space velocity are the volume (in cubic centimeters) of the combination of methane and air fed to the reactor per hour per cubic centimeter of catalyst in the tube. In Examples 1–4 and 28–31, the space velocity is the volume (in cubic centimeters) of the combination of methane and air fed to the reactor per hour per the inside volume (in cubic centimeters) of the reactor. Each of the product selectivity, selectivity for the formation of coupled products (C<sub>2</sub>+), and yield of C<sub>2</sub>+ (the product of methane conversion multiplied by the selectivity for the formation of C<sub>2</sub>+ divided by 100) is reported as mole percent of the carbon in methane in the feed that is converted. C<sub>4</sub>+ in the tables refers to gaseous products containing at least 4 carbon atoms.

In Examples 1–4, the quartz tube was empty, and very little oxygen was consumed even at the highest reaction temperature, leading to little consumption of methane. However, the selectivity for the formation of coupled products (C<sub>2</sub>+), based on the amount of methane consumed, was substantial even though most oxides of carbon appeared as carbon monoxide.

In Examples 5–10, when the tube was filled with pellets of Calsicat D (a product of Mallinckrodt, Inc. of Erie, Pa.), a preferred silica support for the preferred oxidative coupling catalyst, when a reaction temperature of at least 850° C. was employed, nearly all oxygen was consumed, and product selectivity for the formation of coupled product was moderate at 53%. The

conversion to coupled products increased as the reaction temperature was increased, with ethylene predominating as the coupled product. The selectivity for the formation of coupled products also increased at a given reaction temperature as the CH<sub>4</sub>/O<sub>2</sub> mole ratio increased.

When ceramic alumina chips were employed as the tube packing, as indicated in Table 3 for Examples 11–13, oxygen consumption was less, but selectivity for the formation of coupled products (C<sub>2</sub>+) was appreciably better (67–88%) than when Calsicat D was employed as the tube packing. However, high temperatures of the order of 890–945° C. were required to increase oxygen consumption,

#### TABLE 1

Example	1	2	3	4
Tube Packing	Empty Tube			
Reactor Temp. (°C.)	700	800	850	900
Space Velocity	480	480	480	480
CH <sub>4</sub> /O <sub>2</sub> (mole ratio)	9.7/1	9.7/1	9.7/1	9.7/1
O <sub>2</sub> Conversion (mole %)	0.2	4	12	29
CH <sub>4</sub> Conversion (mole %)	—	0.4	1.7	4.5
<u>Product Selectivity</u>				
CO	0	24	34	41
CO <sub>2</sub>	0	0	0	3
C <sub>2</sub> H <sub>4</sub>	0	32	35	39
C <sub>2</sub> H <sub>6</sub>	100	44	31	16
C <sub>2</sub> H <sub>2</sub>	—	—	—	—
C <sub>3</sub> 's	—	—	—	—
C <sub>4</sub> 's+	—	—	—	—
Selectivity to C <sub>2</sub> <sup>+</sup>	100	76	66	55
Yield of C <sub>2</sub> <sup>+</sup>	nil	0.3	1.1	2.5

#### TABLE 2

Example	5	6	7	8	9	10
Tube Packing	Calsicat D Silica					
Reactor Temp. (°C.)	700	800	850	900	900	800
Space Velocity	1200	1200	1200	1200	1000	1000
CH <sub>4</sub> /O <sub>2</sub> (mole ratio)	9.6/1	9.6/1	9.6/1	9.6/1	27/1	27/1
O <sub>2</sub> Conversion (mole %)	4.6	49	94	98+	97+	97+
CH <sub>4</sub> Conversion (mole %)	0.1	4.7	10	12	5.5	4.1
<u>Product Selectivity</u>						
CO	78	44	25	22	19	35
CO <sub>2</sub>	20	20	23	22	15	19
C <sub>2</sub> H <sub>4</sub>	0	16	37	51	62	25
C <sub>2</sub> H <sub>6</sub>	2	20	16	5	4	22
C <sub>2</sub> H <sub>2</sub>	—	—	—	—	—	—
C <sub>3</sub> 's	—	—	—	—	—	—
C <sub>4</sub> 's+	—	—	—	—	—	—
Selectivity to C <sub>2</sub> <sup>+</sup>	2	36	53	56	66	47
Yield of C <sub>2</sub> <sup>+</sup>	nil	1.7	5.3	6.7	3.6	1.9

#### TABLE 3

Example	11	12	13
Tube Packing	Ceramic Chips		
Reactor Temp. (°C.)	851	889	945
Space Velocity	1696	1696	1696
CH <sub>4</sub> /O <sub>2</sub> (mole ratio)	24/1	24/1	24/1
O <sub>2</sub> Conversion (mole %)	14.3	4.1	57
CH <sub>4</sub> Conversion (mole %)	0.4	0.6	3.9
<u>Product Selectivity</u>			
CO	—	3	26
CO <sub>2</sub>	29	9	7
C <sub>2</sub> H <sub>4</sub>	10	27	25
C <sub>2</sub> H <sub>6</sub>	60	58	37
C <sub>2</sub> H <sub>2</sub>	—	—	—
C <sub>3</sub> 's	—	—	—

TABLE 3-continued

Example Tube Packing	11	12 Ceramic Chips	13
C <sub>4</sub> 's+	—	—	—
Selectivity to C <sub>2</sub> <sup>+</sup>	71	88	67
Yield of C <sub>2</sub> <sup>+</sup>	0.3	0.5	2.6

at which temperatures methane reforming, as evidenced by CO formation, increased substantially.

A tube packing of 1 percent by weight of potassium bromide on Calsicat D silica (the silica was dispersed in an aqueous solution of potassium bromide; the solution was evaporated; and the silica was then dried and calcined) was employed in Examples 14–17 (Table 4) and was approximately as active and selective as Calsicat D alone. Celite 408, a diatomaceous silica and a product of Johns-Manville Company, was employed as the tube packing in Examples 18–21 (Table 5) and afforded relatively poor selectivity. Zirconia containing 2 percent by weight of alumina was employed as the tube packing in Examples 22–25 (Table 6) and promoted only formation of carbon oxides. Alpha Alumina was employed as the tube packing in Example 26 (Table 6) and afforded good activity but relatively low selectivity. Mordenite (Norton Zeolon 100) was employed as the tube packing in Example 27 (Table 7) and formed little coupled product but afforded copious coking. A ceramic  $\alpha$ -alumina tube, not containing any tube packing, was employed in Examples 28–31 (Table 7) and was somewhat active at low space velocity and high reaction temperatures and afforded high selectivities for the formation of C<sub>2</sub> and C<sub>3</sub> products. Magnesium aluminum borate, a mixed oxide, was employed as the tube packing in Examples 32–35 (Table 8) and was only moderately active and afforded only moderate selectivity for the formation of coupled products.

In Examples 36–49, several forms of tube packings of lead oxide on various supports were employed. In Examples 36–38 (Table 9), lead oxide on  $\alpha$ -alumina having a surface area of 31 m<sup>2</sup>/g was highly active in catalyzing the conversion of oxygen even at relatively low reaction temperatures, but with relatively poor selectivities of 44–55% for the production of coupled products. By contrast, a low surface area silica (Examples 39–40) was highly selective.

TABLE 4

Example Tube Packing	14	15 1% KBr/Calsicat D Silica	16	17
Reactor Temp. (°C.)	700	800	850	900
Space Velocity	1200	1200	1200	1200
CH <sub>4</sub> /O <sub>2</sub> (mole ratio)	10/1	10/1	10/1	10/1
O <sub>2</sub> Conversion (mole %)	81	98+	98+	98+
CH <sub>4</sub> Conversion (mole %)	6.9	13	14	16
<u>Product Selectivity</u>				
CO	67	34	24	20
CO <sub>2</sub>	18	16	22	21
C <sub>2</sub> H <sub>4</sub>	7	34	38	48
C <sub>2</sub> H <sub>6</sub>	9	15	13	6
C <sub>2</sub> H <sub>2</sub>	0	0	0	0
C <sub>3</sub> 's	0	2	3	4
C <sub>4</sub> 's	—	—	—	—
Selectivity to C <sub>2</sub> <sup>+</sup>	16	51	54	58
Yield of C <sub>2</sub> <sup>+</sup>	1.1	6.6	7.6	9.3

TABLE 5

Example Tube Packing	18	19 Celite 408	20	21
Reactor Temp. (°C.)	700	800	850	900
Space Velocity	1200	1200	1200	1200
CH <sub>4</sub> /O <sub>2</sub> (mole ratio)	10/1	10/1	10/1	10/1
O <sub>2</sub> Conversion (mole %)	42	97+	98+	98+
CH <sub>4</sub> Conversion (mole %)	3.2	6.8	7.2	8.0
<u>Product Selectivity</u>				
CO	53	61	64	63
CO <sub>2</sub>	35	31	26	23
C <sub>2</sub> H <sub>4</sub>	0	3	5	10
C <sub>2</sub> H <sub>6</sub>	13	5	5	4
C <sub>2</sub> H <sub>2</sub>	0	0	0	0
C <sub>3</sub> 's	0	0	0	0
C <sub>4</sub> 's	—	—	—	—
Selectivity to C <sub>2</sub> <sup>+</sup>	13	8	10	14
Yield of C <sub>2</sub> <sup>+</sup>	0.4	0.5	0.7	1.1

TABLE 6

Example Tube Packing	22 ZrO <sub>2</sub> + 2% Al <sub>2</sub> O <sub>3</sub>	23	24	25 $\alpha$ -Alumina	26
Reactor Temp. (°C.)	700	800	850	850	800
Space Velocity	4800	4800	4800	1200	8700
CH <sub>4</sub> /O <sub>2</sub> (mole ratio)	2/1	2/1	2/1	10/1	19.5/1
O <sub>2</sub> Conversion (mole %)	100	100	100	100	100
CH <sub>4</sub> Conversion (mole %)	26	28	33	11	—
<u>Product Selectivity</u>					
CO	20	28	35	64	50.4
CO <sub>2</sub>	81	72	65	36	34.5
C <sub>2</sub> H <sub>4</sub>	0	0	0	0	7.2
C <sub>2</sub> H <sub>6</sub>	0	0	0	0	15.6
C <sub>2</sub> H <sub>2</sub>	0	0	0	0	—
C <sub>3</sub> 's	0	0	0	0	0.6
C <sub>4</sub> 's	—	—	—	—	—
Selectivity to C <sub>2</sub> <sup>+</sup>	0	0	0	0	23
Yield of C <sub>2</sub> <sup>+</sup>	0	0	0	0	—

TABLE 7

Example Tube Packing	Example				
	27	28	29	30	31
	Tube Packing				
	Mordenite	Empty Ceramic Reactor			
Reactor Temp. (°C.)	833	840	885	937	915
Space Velocity	8700	1696	1696	1696	848
CH <sub>4</sub> /O <sub>2</sub> (mole ratio)	20/1	24.1/1	24.1/1	24.1/1	29.1/1
O <sub>2</sub> Conversion (mole %)	92.5	3.8	7.4	19.7	43.2
CH <sub>4</sub> Conversion (mole %)	4.4	nil	0.5	1.8	4.1
<u>Product Selectivity</u>					
CO	51.9	—	—	19.3	22.7
CO <sub>2</sub>	43.9	—	—	—	0.6
C <sub>2</sub> H <sub>4</sub>	—	92.2	20.4	33.6	29.1
C <sub>2</sub> H <sub>6</sub>	4.2	—	64.8	33.9	35.6
C <sub>2</sub> H <sub>2</sub>	—	—	—	—	—
C <sub>3</sub> 's	—	7.8	14.8	11.8	8.3
C <sub>4</sub> 's+	—	—	—	1.4	3.7
Selectivity to C <sub>2</sub> <sup>+</sup>	4.2	100	100	80.7	76.7
Yield of C <sub>2</sub> <sup>+</sup>	0.18	nil	0.5	1.5	3.1

TABLE 8

Example Tube Packing	32	33	34	35
	Magnesium Aluminum Borate			
Reactor Temp. °C.	811	851	846	845
Space Velocity	1695	1695	848	424

TABLE 8-continued

Example	32	33	34	35
	Magnesium Aluminum Borate			
Tube Packing				
CH <sub>4</sub> /O <sub>2</sub> (mole ratio)	22.6/1	22.6/1	24.9/1	30.1/1
O <sub>2</sub> Conversion (mole %)	39.9	38.0	63.4	98.0
CH <sub>4</sub> Conversion (mole %)	2.2	3.2	3.8	3.4
<u>Product Selectivity</u>				
CO	46.7	48.7	40.2	49.1
CO <sub>2</sub>	12.4	5.4	7.6	8.0
C <sub>2</sub> H <sub>4</sub>	6.0	10.5	19.3	22.3
C <sub>2</sub> H <sub>6</sub>	28.6	28.2	25.3	15.6
C <sub>2</sub> H <sub>2</sub>	—	4.6	3.5	1.7
C <sub>3</sub> 's	2.2	1.6	3.2	2.8
C <sub>4</sub> 's+	4.2	1.0	1.0	0.4
Selectivity to C <sub>2</sub> <sup>+</sup>	41.0	45.9	52.3	42.8
Yield of C <sub>2</sub> <sup>+</sup>	0.9	1.5	2.0	1.5

Examples 39–49 (Table 9) demonstrate the surprising influence on the oxidative coupling reaction of the physical properties of the support employed in the lead oxide catalyst. By contrast to the relatively high surface area supports employed in Examples 47–49, lead oxide on Calsicat D, a low surface area silica, afforded very high conversion of oxygen in all cases, with selectivities for the formation of coupled products in excess of 90% at CH<sub>4</sub>/O<sub>2</sub> mole ratios of at least 19/1. Furthermore, in such examples, the selectivities for the formation of coupled products were maintained at levels of greater than 75% even at the CH<sub>4</sub>/O<sub>2</sub> ratio of 5/1. The high surface area silica tube packing employed in Examples 47–49 afforded selectivities for the formation of coupled products that were comparable to those for the  $\alpha$ -alumina packing employed in Examples 36–38.

To establish the influence of the surface area of the support used in preparing the oxidative coupling catalyst and of the conditions under which such support is calcined prior to impregnation, several samples of a high surface area silica (Philadelphia Quartz PQ-CD107G SiO<sub>2</sub>) with a surface area of 239 m<sup>2</sup>/gm were calcined under various conditions (indicated in Table 10), converted to catalysts, each containing 20% by weight of PbO, by precipitation of a lead compound from an aqueous solution of its nitrate in the presence of the silica and further calcination in air at about 600° C. to form the PbO-impregnated silica, and then evaluated as catalysts in the oxidative coupling reaction in Examples 50–54. In each evaluation, the following conditions were employed: a reaction temperature of 750–850° C., a space velocity of 6600 cc/hr/cc, and a CH<sub>4</sub>/O<sub>2</sub> mole ratio of 20. The experimental parameters and results presented in Table 10 for Examples 50–54 illustrate that, as the surface area of the silica is decreased, until the surface area fell to about 21 m<sup>2</sup>/gm, there was a progressive increase in the selectivity for the production of coupled products.

TABLE 9

Example	Example				
	36	37	38	39	40
Tube Packing					
	20% PbO on				
	$\alpha$ -Alumina				Calsicat D Silica (24 m <sup>2</sup> /g)
Reactor Temp. (°C.)	757	818	803	733	830
Space Velocity	8700	8700	8700	6600	6600
CH <sub>4</sub> /O <sub>2</sub> (mole ratio)	20/1	19/1	5.1/1	20/1	20/1

TABLE 9-continued

O <sub>2</sub> Conversion (mole %)	100	100	100	37.9	44.1
<u>Product Selectivity</u>					
CO	—	1.2	—	—	—
CO <sub>2</sub>	48.0	44.2	55.6	37.4	9.7
C <sub>2</sub> H <sub>4</sub>	17.6	26.0	21.8	2.0	20.5
C <sub>2</sub> H <sub>6</sub>	32.8	26.2	20.8	60.4	68.0
C <sub>2</sub> H <sub>2</sub>	—	—	—	—	—
C <sub>3</sub> 's	1.5	2.4	1.8	0.2	1.8
C <sub>4</sub> 's	—	—	—	—	—
Selectivity to C <sub>2</sub> <sup>+</sup>	51.9	54.6	44.4	62.6	90.3
<u>Example</u>					
	41	42	43	44	45
Tube Packing					
	20% PbO on Calsicat D Silica (24 m <sup>2</sup> /g)				
Reactor Temp. (°C.)	835	852	872	896	915
Space Velocity	3300	3300	6600	3300	1320
CH <sub>4</sub> /O <sub>2</sub> (mole ratio)	21/1	21/1	19/1	20/1	10.3/1
O <sub>2</sub> Conversion (mole %)	76.8	88.0	65.8	92.3	100
CH <sub>4</sub> Conversion (mole %)			6.8	8.5	13.4
<u>Product Selectivity</u>					
CO	—	—	—	—	6.6
CO <sub>2</sub>	9.8	9.7	8.5	9.6	14.2
C <sub>2</sub> H <sub>4</sub>	31.4	35.8	30.8	37.4	43.6
C <sub>2</sub> H <sub>6</sub>	57.0	52.2	53.2	42.4	26.2
C <sub>2</sub> H <sub>2</sub>	—	—	2.7	2.8	2.0
C <sub>3</sub> 's	1.8	2.4	4.8	7.5	7.2
C <sub>4</sub> 's	—	—	—	0.4	6.8
Selectivity to C <sub>2</sub> <sup>+</sup>	90.2	90.4	91.5	90.5	85.8
Yield of C <sub>2</sub> <sup>+</sup>			6	8	11
<u>Example</u>					
	47	48	49		
Tube Packing					
	17% PbO on High Surface Area Silica (245 m <sup>2</sup> /g)				
Reactor Temp. (°C.)		740	740	740	
Space Velocity		13,040	6135	1341	
CH <sub>4</sub> /O <sub>2</sub> (mole ratio)		10/1	10/1	10/1	
O <sub>2</sub> Conversion (mole %)		19.9	26.1	53.0	
<u>Product Selectivity</u>					
CO		—	—	1.6	
CO <sub>2</sub>		48.5	41.4	39.4	
C <sub>2</sub> H <sub>4</sub>		6.9	8.2	16.3	
C <sub>2</sub> H <sub>6</sub>		44.3	50.2	42.0	
C <sub>2</sub> H <sub>2</sub>		—	—	—	
C <sub>3</sub> 's		0.3	0.2	0.6	
C <sub>4</sub> 's		—	—	—	
Selectivity to C <sub>2</sub> <sup>+</sup>		51.5	58.6	58.9	

TABLE 10

Example	Conditions of Calcination Before Impregnation	Surface Area (m <sup>2</sup> /gm)	Selectivity to C <sub>2</sub> <sup>+</sup>
50	2 hrs. at 650° C.	239	45
51	8 hrs. at 830° C.	179	66
52	8 hrs. at 920° C.	116	85
53	8 hrs. at 970° C.	21	Low Activity
54	4 hrs. at 1000° C.	<2	Inactive

The catalyst prepared in Example 52 was evaluated in Examples 55–59 as a catalyst for the oxidative coupling reaction under varying conditions of reaction temperature and space velocity. As indicated by the experimental parameters and results presented for Examples 55–59 in Table 11, the degree of oxygen conversion increased as the reaction temperature was increased at a constant space velocity and as the space velocity was decreased.





TABLE 15-continued

Example	108	109	110	111	112	113	114	115	116	117	118
Tube Packing	20% PbO-Norton SiO <sub>2</sub> Containing 1.66% MgO										
C <sub>2</sub> H <sub>4</sub> /C <sub>2</sub> H <sub>6</sub> (mole ratio)	0.283	0.565	0.471	0.734	1.028	1.319	1.495	0.465	0.467	0.601	0.555

Additional experiments have shown that the incorporation of lithium, potassium or cesium also affords improved selectivities of the catalysts in the oxidative coupling reaction. By contrast, incorporation of an alkaline earth metal component into the catalyst was not beneficial. Higher C<sub>2</sub>H<sub>4</sub>:C<sub>2</sub>H<sub>6</sub> mole ratios are desirable in order to increase the yield of aromatics formed by the oligomerization of ethylene in a subsequent step, as described hereinbelow in connection with Examples 169-187.

The level of metal component on the support was found to be important within broad ranges. As can be seen from Examples 119-127, all levels of lead oxide on Calscat D silica were effective when compared with Caliscat D silica without lead oxide (Examples 5-10). However, the low levels of lead oxide, particularly 5.9%, tend to form some carbon monoxide at 800° C. as did the base silica itself, while the higher levels of lead oxide made less or none at all.

One problem with the use of lead oxide on silica is its tendency to deactivate. As illustrated in Table 10, the support must be calcined before impregnating with the reducible metal component to obtain a selective catalyst. However, it is also necessary to calcine the catalyst containing the reducible metal component at high temperature in the presence of oxygen to maintain a highly stable catalyst. Examples 128-136 illustrate the influence of calcination after impregnation on catalyst performance. Without air calcination (Examples 128-130), activity and selectivity were high, but prolonged use of the catalyst above 800° C. caused the catalyst to deactivate. When calcined in air at 1000° C. for 16 hours (Examples 131-133), the catalyst showed surprisingly good activity and selectivity and could be used for prolonged periods with little loss of activity. Calcination in air at 1000° C. for sixty hours (Examples 134-136) likewise provided a highly selective and stable catalyst, although

TABLE 16

Example	119	120	121	122	123	124	125	126	127
Tube Packing	Lead Oxide on Calscat D Silica								
PbO level (wt %)	5.9%			11.1%			33.3%		
Reaction Temp. (°C.)	747	802	839	757	801	837	757	801	837
Space Velocity	1695	1695	1695	1695	1695	1695	1695	1695	1695
CH <sub>4</sub> /O <sub>2</sub> (mole ratio)	23.5/1	23.5/1	23.5/1	23.7/1	23.7/1	23.7/1	24.0/1	24.0/1	24.0/1
O <sub>2</sub> Conversion (mole %)	72.2	99.1	99.3	60.8	69.0	99.1	47.7	67.3	99.0
CH <sub>4</sub> Conversion (mole %)	3.8	7.3	8.0	2.8	4.4	7.6	3.7	5.4	7.2
<u>Product Selectivity</u>									
CO	—	2.8	1.2	—	0.9	1.7	—	—	—
CO <sub>2</sub>	29.1	13.4	10.6	38.4	21.9	12.6	13.6	10.2	10.1
C <sub>2</sub> H <sub>4</sub>	14.9	29.9	38.6	7.7	16.6	31.1	18.5	29.2	37.1
C <sub>2</sub> H <sub>6</sub>	54.2	50.4	44.4	50.9	58.8	51.1	65.7	57.1	46.9
C <sub>2</sub> H <sub>2</sub>	—	0.9	1.4	—	0.1	0.9	0.2	0.4	0.7
C <sub>3</sub> 's	1.8	2.6	3.4	3.0	1.7	2.6	2.1	2.9	3.6
C <sub>4</sub> 's and higher	—	0.1	0.3	—	—	—	—	0.2	—
Selectivity to C <sub>2</sub> <sup>+</sup>	70.9	83.9	88.1	61.6	77.2	85.7	86.5	89.8	88.3
Yield of C <sub>2</sub> <sup>+</sup>	2.7	6.1	7.0	1.7	3.4	6.5	3.2	4.8	6.4

TABLE 17

Example	128	129	130	131	132	133	134	135	136
Calcination Temp. (°C.)	600	600	600	1000	1000	1000	1000	1000	1000
Calcination Time (hr)	16	16	16	16	16	16	60	60	60
Air	no	no	no	yes	yes	yes	yes	yes	yes
Reaction Temp. (°C.)	721	807	822	745	831	856	723	825	863
Space Velocity	1700	1700	1700	1700	1700	1700	1700	1700	1700
CH <sub>4</sub> /O <sub>2</sub> (mole ratio)	18.5/1	18.5/1	18.5/1	23.4/1	23.4/1	23.4/1	24.2/1	24.2/1	24.3/1
O <sub>2</sub> Conversion (mole %)	71.1	95.2	95.0	68.7	99.5	99.5	9.7	68.5	99.1
CH <sub>4</sub> Conversion (mole %)	—	—	—	4.5	9.0	8.2	0.7	5.5	7.4
<u>Product Selectivity</u>									
CO	—	—	1.8	—	1.5	—	—	2.5	3.8
CO <sub>2</sub>	21.1	14.0	12.7	20.9	9.7	10.2	15.2	9.5	8.5
C <sub>2</sub> H <sub>4</sub>	14.8	36.3	42.2	17.8	34.1	43.2	5.4	31.8	42.1
C <sub>2</sub> H <sub>6</sub>	39.4	44.7	30.9	59.6	41.7	39.9	72.0	52.0	39.9
C <sub>2</sub> H <sub>2</sub>	—	—	0.7	—	0.4	—	—	1.3	1.7
C <sub>3</sub> 's	4.1	3.2	4.7	1.6	2.9	3.8	7.5	2.9	3.7
C <sub>4</sub> 's and higher	20.7	1.7	7.1	—	11.4	1.0	—	—	0.4
Selectivity to C <sub>2</sub> <sup>+</sup>	79.0	85.9	85.6	79.0	90.5	87.9	84.9	88.0	87.8

TABLE 17-continued

Example	128	129	130	131	132	133	134	135	136
Yield of C <sub>2</sub> <sup>+</sup>				3.6	8.1	7.2	5.9	4.8	6.5

some of its original activity was lost, particularly at low coupling temperatures. It is believed that lead oxide in calcination reacts with the silica base to form some form of lead silicate. In the presence of air this compound presumably is maintained in its highest valence state.

The conditions employed to calcine the oxidative coupling catalysts employed in Examples 5-27 and 32-187 are summarized in Table 18.

Other lead compounds have been shown to give good selectivities for the formation of coupled products, depending on the nature of the anion. Lead sulfate (Examples 137-141) was relatively unattractive until it was exposed to prolonged reaction conditions. During this period, SO<sub>2</sub> was evolved making a new and more selective species. Lead sulfide (Examples 142-144) was active from the beginning and afforded high selectivity for the formation of coupled products but tended to deactivate with time. Lead tungstate (Examples 145-147) was moderately selective at low temperatures. Lead molybdate (Examples 148-149) was much less selective even at low temperatures. In each of Examples 137-149, the lead compound was supported on a Calsicat D support. Preferred anions are those that can decompose to form a lead oxide type of compound.

Catalysts containing compounds of reducible metals other than lead are less selective when tested in the oxidative coupling reaction under similar conditions. For example, vanadia on Calsicat D silica afforded only

TABLE 18

Example	Conditions of Calcination Before Impregnation	Surface Area (m <sup>2</sup> /gm) Before Impregnation	Conditions of Calcination After Impregnation
5-10 <sup>1</sup>	8 hrs at 1000° C.	24	
11-13 <sup>1</sup>	used as received	<5	
14-17	used as received	24	
18-21 <sup>1</sup>	2 hrs at 600° C.	<5	
22-25 <sup>1</sup>	2 hrs at 600° C.	44	
26 <sup>1</sup>	2 hrs at 600° C.	—	
27 <sup>1</sup>	2 hrs at 600° C.	—	
32-35 <sup>1</sup>	2 hrs at 743° C.	—	
36-38	—	4	2 hrs at 600° C.
39-46	used as received	24	2 hrs at 600° C.
47-49	used as received	245	2 hrs at 600° C.
50	2 hrs at 650° C.	239	2 hrs at 600° C.
51	8 hrs at 830° C.	179	2 hrs at 600° C.
52	8 hrs at 920° C.	116	2 hrs at 600° C.
53	8 hrs at 970° C.	21	2 hrs at 600° C.
54	4 hrs at 1000° C.	<2	2 hrs at 600° C.
55-59	8 hrs at 920° C.	116	2 hrs at 600° C.
60-118	2-3 hrs at 550-660° C.	—	2 hrs at 600° C.
119-127	used as received	24	2 hrs at 600° C.
128-130	used as received	24	16 hrs at 600° C.
131-133	used as received	5 <sup>2</sup>	16 hrs at 1000° C.
134-136	used as received	4 <sup>2</sup>	60 hrs at 1000° C.
137-168	used as received	24	2 hrs at 600° C.
181-188	used as received	24	2 hrs at 600° C.

<sup>1</sup>Not impregnated

<sup>2</sup>Surface area after impregnation

TABLE 19

	Example													
	137	138	139	140	141	142	143	144	145	146	147	148	149	
	Tube Packing 20% PbSO <sub>4</sub>					Lead Compound 20% PbS			Tube Packing 20% PbWO <sub>4</sub> 20% PbMoO <sub>4</sub>					
Reaction Temp. (°C.)	715	756	803	842	830	757	805	858	742	807	879	763	863	
Space Velocity	1695	1695	1695	1695	3390	1690	1690	1690	3390	3390	3390	1695	1695	
CH <sub>4</sub> /O <sub>2</sub> (mole ratio)	22.7/1	22.7/1	22.7/1	22.8/1	22.1/1	23.0/1	23.1/1	23.1/1	22.3/1	22.3/1	22.3/1	23.8/1	23.8/1	
O <sub>2</sub> Conversion (mole %)	99.4	99.3	99.4	99.2	99.4	82.7	99.0	99.4	62.4	99.3	99.1	99.4	99.0	
CH <sub>4</sub> Conversion (mole %)	8.5	7.3	6.9	7.3	8.3	6.4	7.3	8.7	3.2	5.4	7.3	3.6	4.7	
<b>Product Selectivity</b>														
CO	—	—	0.3	1.7	3.4	—	—	—	—	7.4	44.5	6.7	43.9	
CO <sub>2</sub>	58.5	31.9	19.9	17.0	12.2	20.5	13.1	10.3	36.5	36.1	26.7	65.5	40.3	
C <sub>2</sub> H <sub>4</sub>	7.3	16.7	30.5	42.7	32.9	19.4	32.6	42.2	8.1	12.3	5.4	2.6	2.7	
C <sub>2</sub> H <sub>6</sub>	28.6	36.7	45.5	32.8	47.6	55.6	51.2	34.6	51.1	42.4	21.4	24.6	10.8	
C <sub>2</sub> H <sub>2</sub>	—	—	0.6	0.5	0.7	0.1	0.4	2.3	1.5	—	0.9	—	1.6	
C <sub>3</sub> 's	1.0	2.4	2.3	4.0	2.9	1.8	2.8	4.3	2.2	1.8	1.0	0.6	0.7	
C <sub>4</sub> 's+	4.6	12.3	0.9	1.3	0.2	1.2	—	6.4	0.7	—	—	—	—	
Selectivity to C <sub>2</sub> <sup>+</sup>	41.5	68.1	79.8	81.3	84.3	78.1	87.0	89.8	63.6	56.5	28.7	27.8	15.8	
Yield of C <sub>2</sub> <sup>+</sup>	3.5	5.0	5.0	5.9	7.0	5.0	6.4	7.8	1.9	3.1	2.1	1.0	0.7	

a 22% selectivity for the formation of coupled products. Manganese oxide on Calsicat D silica afforded 50-64% selectivity for the formation of coupled products. Indium oxide on Calsicat D silica afforded a 31-45% selectivity for the formation of coupled products.

#### EXAMPLES 150-155

All of the examples of the oxidative coupling reaction presented in Examples 1-149 were performed using a

once-through operational mode, with no attempt being made to recover and recycle the unreacted feedstock alkane. In order to increase the conversion of the feedstock alkane and the yield of desired products therefrom, it is desirable to recycle unused feedstock alkane. However, the use of simple recycle of the entire product mixture formed in the oxidative coupling reaction is not particularly advantageous as shown in Examples 150-155. Examples 150-155 were performed using the same general procedure as used in Examples 39-46, except that in Examples 154-155 the product was recycled. The catalyst employed in Examples 150-155 was a

Calsicat D silica support (that had not been calcined prior to impregnation) containing 20% by weight of PbO that was calcined for 2 hours at 600° C. after impregnation.

Examples 150–153 show the performance of a lead oxide catalyst on Calsicat D silica in a once-through mode. As is seen, even at the lowest CH<sub>4</sub>/O<sub>2</sub> mole ratio of 5.2/1 (Example 153), the selectivity for the formation of coupled products was respectable, but the conversion of methane and yield of coupled products were at best only about 19% and 14%, respectively.

Surprisingly, however, when the entire gaseous product mixture from the oxidative coupling reaction was recycled to the oxidative coupling step (Examples 154–155), selectivity for the formation of coupled products dropped drastically into the range of 42–61%, even with high mole ratios of CH<sub>4</sub>/O<sub>2</sub> in the total incoming gas, and the yield of desired product (obtained as the product of the CH<sub>4</sub> conversion multiplied by the selectivity for the formation of coupled products, divided by 100) was no better than with once-through operations.

#### EXAMPLES 156–168

Examples 156–168 involve a systematic study to find the components in recycle gas that are responsible for this undesirable effect illustrated in Examples 154–155. Examples 156–168 were performed using the same general

TABLE 20

Example	150	151	152	153	154	155
Reaction Temp. (°C.)	829	896	915	914	836	836
Space Velocity	6600	3300	1320	1320	1690	1690
Recycle CH <sub>4</sub> /O <sub>2</sub> (mole ratio) in makeup feed	18.7/1	No 19.9/1	No 10.3/1	No 5.2/1	Yes 8.4/1	Yes 8.4/1
CH <sub>4</sub> /O <sub>2</sub> (mole ratio) in total feed	18.7/1	19.9/1	10.3/1	5.2/1	33.2/1	24.5/1
O <sub>2</sub> Conversion (mole %)	33.7	92.3	100.0	88.7	96.4	94.9
CH <sub>4</sub> Conversion (mole %)	3.4	8.5	13.4	18.7	9.5	22.0
Product Selectivity						
CO	0.0	0.0	0.0	6.6	6.5	6.7
CO <sub>2</sub>	8.3	9.6	14.2	18.3	32.9	51.1
C <sub>2</sub> H <sub>4</sub>	19.7	37.4	43.6	30.2	32.7	25.3
C <sub>2</sub> H <sub>6</sub>	70.4	42.4	26.2	20.2	14.0	9.8
C <sub>2</sub> H <sub>2</sub>	0.0	2.8	2.0	0.0	0.7	0.6
C <sub>3</sub> 's	1.7	7.5	7.2	19.5	4.7	3.2
C <sub>4</sub> 's	0.0	0.4	6.8	5.6	8.0	2.7
Selectivity to C <sub>2</sub> <sup>+</sup>	91.8	90.5	85.8	75.5	60.1	41.6
Yield of C <sub>2</sub> <sup>+</sup>	3.1	7.7	11.5	14.1	5.7	9.2

procedure as used in Examples 39–46, except as indicated herein. The catalyst employed in Examples 156–168 was a Calsicat D silica support (that had not been calcined prior to impregnation) containing 20% by weight of PbO that was calcined for 2 hours at 600° C.

after impregnation. By spiking methane feed to the oxidative coupling reaction with nitrogen, carbon monoxide, carbon dioxide and water, it was observed that none of these materials had a deleterious effect. Residual olefins and acetylene in the recycle gas, however, did have an undesirable effect in the oxidative coupling reaction. Ethane itself did not. The effect of ethane in the oxidative coupling reaction is shown in Examples 156–161. A blend of 10% ethane and 90% methane showed a surprising increase of both selectivity and yield for ethylene and higher products. Even a 100% ethane feedstock was converted to unsaturates in high selectivity and yield. Accountability of carbons across the system was essentially 100%, indicating little tendency to form coke. On the other hand, the presence of ethylene in the feedstock to the oxidative coupling reactor had a deleterious effect, even at levels of 1% in methane, as shown in Examples 162–168. Of particular concern was the observation that accountability of carbons across the system was poor, as a result of coke formation. Thus, in order to increase the degree of conversion of the feedstock alkane and the yield of the desired products therefrom, the recycle gas must be substantially free of ethylene and other higher unsaturates to preserve the high selectivity of an oxidative coupling catalyst for methane coupling, but it is advantageous that ethane is present in the feed or recycle.

#### EXAMPLES 169–188

It was surprisingly observed that certain acid catalysts were able to remove ethylene and higher unsaturates from very dilute methane streams even at atmospheric pressure and that this reaction gave rise to high yields of recoverable aromatic hydrocarbons. While it had been

TABLE 21

	Examples					
	156	157	158	159	160	161
	Feed					
	10% C <sub>2</sub> H <sub>6</sub> in CH <sub>4</sub>			100% C <sub>2</sub> H <sub>6</sub>		
Reaction Temp. (°C.)	783	838	847	739	787	823
Space Velocity	6600	6600	3300	6600	6600	6600
CH <sub>4</sub> /O <sub>2</sub> (mole ratio)	16.8/1	16.8/1	17.6/1	—	—	—
C <sub>2</sub> H <sub>6</sub> /O <sub>2</sub> (mole ratio)	1.76/1	1.76/1	1.89/1	11.5	11.5	5.4
O <sub>2</sub> Conversion (mole %)	30.0	85.3	100	59.2	100	100
C <sub>2</sub> H <sub>6</sub> Conversion (mole %)	19.2	44.2	66.5	9.7	27.3	62.5
Product Selectivity						
CO	—	—	—	0.15	2.1	3.9
CO <sub>2</sub>	6.9	5.4	3.3	1.3	0.6	0.8
CH <sub>4</sub>	—	—	—	2.4	2.9	5.2
C <sub>2</sub> H <sub>4</sub>	89.6	89.2	86.2	92.0	88.2	84.0
C <sub>2</sub> H <sub>6</sub>	—	—	—	—	—	—
C <sub>2</sub> H <sub>2</sub>	—	0.8	2.3	—	2.5	3.0
C <sub>3</sub> 's	3.5	4.7	6.3	4.1	1.8	2.2
C <sub>4</sub> 's	—	—	2.0	—	2.0	0.8
Selectivity to C <sub>2</sub> <sup>+</sup>	93.1	94.7	96.8	96.1	94.5	90.0
Yield of C <sub>2</sub> <sup>+</sup>	17.9	41.9	64.3	9.3	25.8	56.3

TABLE 22

Example	162	163	164	165	166	167	168
Feed, % C <sub>2</sub> H <sub>4</sub> in CH <sub>4</sub>	0	0.8	1.4	10	10	100	100
Temp. (°C.)	815	814	811	746	795	733	836
Space Velocity	6600	6600	6600	6600	6600	6600	3300
CH <sub>4</sub> /O <sub>2</sub>	24.1/1	25.9/1	27.3/1	18.0/1	18.0/1	—	—



TABLE 22-continued

Example	162	163	164	165	166	167	168
(mole ratio)							
C <sub>2</sub> H <sub>4</sub> /O <sub>2</sub>	—	—	—	2.3/1	2.3/1	16.8/1	2.3/1
(mole ratio)							
O <sub>2</sub> Conversion	52.6	64.4	67.3	85.0	99.7	71.8	100
(mole %)							
C <sub>2</sub> H <sub>4</sub> Conv. (mole %)	—	—	—	14.7	20.6	4.2	62.6
<u>Product Selectivity</u>							
CO	—	—	—	1.4	0.1	44.1	29.0
CO <sub>2</sub>	8.5	15.6	18.1	25.1	21.9	?	16.1
CH <sub>4</sub>	—	—	—	—	—	9.0	16.1
C <sub>2</sub> H <sub>4</sub>	28.0	15.1	2.4	—	—	—	—
C <sub>2</sub> H <sub>6</sub>	47.8	47.9	61.1	26.0	27.8	7.9	4.8
C <sub>2</sub> H <sub>2</sub>	—	—	4.3	4.7	6.2	5.9	1.9
C <sub>3</sub> 's	15.8	17.3	8.9	9.9	13.8	26.1	5.6
C <sub>4</sub> 's+	—	—	5.2	32.9	30.3	7.0	20.9
Selectivity to C <sub>2</sub> <sup>+</sup>	91.6	80.3	81.9	73.5	78.1	46.9	33.2

known that metal-exchanged zeolites do oligomerize ethylene to form higher molecular weight olefins under pressure, we found that such catalysts are ineffective under conditions of low pressure and low concentration. Similarly, an alumina catalyst containing vanadium oxide and palladium and reported by A. B. Evin, et al, *J. of Catalysis*, 30, 109-117 (1973) for the oxidative conversion of ethylene to acetaldehyde, was employed in the oligomerization reaction with a synthetic mixture containing nitrogen, oxygen, methane, acetylene, ethylene, ethane and traces of C<sub>3</sub> and C<sub>4</sub> paraffins and olefins, but was found to convert only 14-56% of the ethylene at very low space velocities. When used with the same mixture in the oligomerization reaction, concentrated sulfuric acid was effective only for the conversion of higher olefins.

Only zeolitic materials in the acid-exchanged form showed appreciable activity in the oligomerization reaction. A number of the most effective materials are shown in Examples 169-180. Examples 169-176 involve a catalyst which is a composite of 35 weight percent of alumina and 65 weight percent of one of two acidic borosilicate molecular sieves made in accordance with preparations disclosed in Haddid, European Patent Application No. 82303246.1. A borosilicate sieve of relatively low acidity was employed in Examples 169-172. It gave good conversion of ethylene at low space velocities, complete acetylene conversion at all space velocities tested and complete or nearly complete conversion of propylene under most conditions. Although products above C<sub>5</sub> were not measured in these studies, the buildup of higher hydrocarbons was observed. A borosilicate of stronger acidity was employed in Examples 172-176 and was more effective than the less acidic borosilicate, giving 80-90% conversion of ethylene over a wide temperature range at a higher space velocity. ZSM-5, the strongest acidic zeolitic material tested, was employed in Examples 177-180 and was especially effective, giving 95-100% conversion of ethylene at space velocities in the range of 269-1440. Water was found not to be detrimental to the olefin conversion as indicated by Examples 175-176 and 179-180.

To show the effect of the oligomerization of unsaturates on the effectiveness of recycle to the oxidative coupling reaction, a packed column of H-ZSM-5 was employed in Examples 181-189 at the outlet of the oxidative coupling reactor to oligomerize the unsaturates in the product stream, higher products were largely removed with a dry-ice acetone trap, and the remaining gases were recycled back to the oxidative

coupling reactor. The oxidative coupling catalyst employed was a Calscat D silica support (which had not been calcined prior to being impregnated) containing 20 percent by weight of lead oxide and which had been calcined in air at about 600° C. for 2 hours after impregnation.

By comparison to the results of Example 155 where olefins in the feed to the oxidative coupling reactor were not oligomerized, in Examples 181-188, there was a noticeable improvement in methane conversion, selectivity for the production of coupled products and yield of coupled products in the oxidative coupling reaction. Furthermore, liquids in large quantities were condensed out of the system.

To demonstrate that small amounts of oligomerization products and higher molecular weight coupled products remaining in the recycle after oligomerization and after the dry ice-acetone trap were detrimental to the oxidative coupling reaction, the recycle stream was passed through a bed of granular coconut charcoal after passing through the dry-ice trap and before being returned to the oxidative coupling reactor. The effect of this is seen in Examples 185-188. By the simple addition of a charcoal bed, methane conversions, selectivities for the formation of coupled products and yields of coupled products increased to 63-82%, 78-85% and 53-67%, respectively.

TABLE 23

Example	169	170	171	172
Temp. (°C.)	396	353	337	321
Speed Velocity	191	96	49	44
<u>Feed</u>				
Component	Percent	Percent Removed in Product <sup>1</sup>		
N <sub>2</sub>	48.8	0	0	0
CH <sub>4</sub>	47.0	0.4	0	0.9
CO <sub>2</sub>	0.49	0.7	-0.9	0.2
O <sub>2</sub>	0.99	0.3	-0.8	-0.5
C <sub>2</sub> H <sub>4</sub>	1.01	34.6	57.7	78.5
C <sub>2</sub> H <sub>6</sub>	1.01	1.7	0.4	0.2
C <sub>2</sub> H <sub>2</sub>	0.13	100	81.7	100
C <sub>3</sub> H <sub>8</sub>	0.10	0	0	0
C <sub>3</sub> H <sub>6</sub>	0.11	16.7	84.4	100
I-C <sub>4</sub>	0.11	-72.7	-47.8	-83.7
N-C <sub>4</sub>	0.06	-116	-59.7	-43.5
C <sub>4</sub> +	0.27	-19.1	-1.6	6.4
Example	173	174	175 <sup>2</sup>	176 <sup>2</sup>
Temp. (°C.)	296	317	310	365
Space Velocity	360	360	360	360
<u>Feed</u>				
Component	Percent	Percent Removed in Product <sup>1</sup>		

TABLE 23-continued

N <sub>2</sub>	48.9	0	0	0	0
CH <sub>4</sub>	47.0	-0.8	-0.9	0.4	-0.3
CO <sub>2</sub>	0.50	5.6	6.8	-20.5	-14.0
O <sub>2</sub>	1.00	-1.0	-1.0	-0.8	-0.6
C <sub>2</sub> H <sub>4</sub>	1.00	79.9	89.9	88.5	87.3
C <sub>2</sub> H <sub>6</sub>	1.00	-1.8	-2.8	-2.3	-3.3
C <sub>2</sub> H <sub>6</sub>	0.01	100	100	100	100
C <sub>3</sub> H <sub>8</sub>	0.10	-97.1	-150	-74.8	-150
C <sub>3</sub> H <sub>6</sub>	0.10	100	93.5	100	100
I-C <sub>4</sub>	0.10	-79.6	-94.7	-124.1	-94.5
N-C <sub>4</sub>	0.10	24.5	22.0	18.9	19.7
C <sub>4</sub> +	0.10	-9.6	-14.5	-29.9	31.4
Example		177	178	179 <sup>2</sup>	180 <sup>2</sup>
Temp. (°C.)		296	301	309	292
Space Velocity		360	1440	720	1440

Feed		Percent Removed in Product <sup>1</sup>			
Component	Percent				
N <sub>2</sub>	48.9	0	0	0	0
CH <sub>4</sub>	47.0	-0.8	-0.3	0.5	0.2
CO <sub>2</sub>	0.50	23.7	11.7	2.3	0.7
O <sub>2</sub>	1.00	-0.4	-0.3	1.6	-1.4
C <sub>2</sub> H <sub>4</sub>	1.00	100	95.0	99.0	96.1
C <sub>2</sub> H <sub>6</sub>	1.00	-1.3	-0.7	-2.4	-1.7
C <sub>2</sub> H <sub>6</sub>	0.01	100	100	100	100
C <sub>3</sub> H <sub>8</sub>	0.10	-142	-183	-150	-138
C <sub>3</sub> H <sub>6</sub>	0.10	100	100	100	100
I-C <sub>4</sub>	0.10	-172	-152	-179	-161
N-C <sub>4</sub>	0.10	30.5	17.6	30	30.2
C <sub>4</sub> +	0.10	-14.5	-30.3	-37.8	-2.3

<sup>1</sup>A negative value indicates an increase in that component.

<sup>2</sup>Water was added with the feed at about 10 moles per mole of ethylene.

TABLE 24

Example	155	181	182	183	184	185	186	187	188
	Special Conditions	Without Charcoal				With Charcoal			
Oxid. Coup.	836	806	824	810	853	854	858	847	809
Temp. (°C.)									
Oxid. Coup.	1690	1690	1690	2618	1960	2618	2618	1960	1940
Space Velocity									
Recycle	yes	yes	yes	yes	yes	yes	yes	yes	yes
Oligomerization	no	yes	yes	yes	yes	yes	yes	yes	yes
Olig. Temp. (°C.)	—	285	285	285	285	285	285	285	285
Olig. Space Velocity	—	~1400	~1400	~1400	~1400	~1400	~1400	~1400	~1400
Velocity									
CH <sub>4</sub> /O <sub>2</sub> (mole ratio) in makeup feed	8.4/1	4.2/1	4.0/1	2.3/1	1.43/1	1.92/1	1.92/1	1.52/1	1.47/1
CH <sub>4</sub> /O <sub>2</sub> (mole ratio) in total feed	24.5/1	23.2/1	26.1/1	18.3/1	16.4/1	13.6/1	13.6/1	14.3/1	7.2/1
O <sub>2</sub> Conversion (mole %)	94.9	94.4	95.0	99.5	99.4	96.8	99.1	99.4	98.6
CH <sub>2</sub> Conversion (mole %)	22.0	32.2	27.9	49.1	62.9				
CH <sub>4</sub> Conversion (mole %)						63.1	64.9	72.5	81.6
Product Selectivity									
CO	6.7	2.2	0.9	0.8	1.2	0.6	0.8	0.7	0.0
CO <sub>2</sub>	51.1	17.2	15.8	30.5	35.2	14.8	17.8	21.6	17.8
C <sub>2</sub> H <sub>4</sub>	25.3	0.0	0.1	0.0	0.2	0.2	0.2	0.1	0.0
C <sub>2</sub> H <sub>6</sub>	9.8	7.6	7.6	5.9	3.1	3.3	3.3	2.6	1.7
C <sub>2</sub> H <sub>2</sub>	0.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C <sub>3</sub> 's	3.7	0.9	1.8	1.1	0.7	0.5	0.6	0.4	0.4
C <sub>4</sub> 's	2.7	3.8	8.8	2.8	2.1	2.1	4.1	1.0	0.0
Liquids	—	68	66	59	57	79	53	56	67
Selectivity to C <sub>2</sub> <sup>+</sup>	42.1	80.6	83.3	68.8	63.6	84.6	81.4	77.7	82.2
Yield of C <sub>2</sub> <sup>+</sup>	9	26	23	34	40	53	53	56	67

## EXAMPLE 189

Since air is added to the system in the oxidative coupling step, a slip stream of the recycle gas is vented to prevent a buildup of nitrogen in the gas that is recycled to the oxidative coupling step. The slip stream which is vented contains about 10–20% of the methane originally charged to the reactor. We have found that, by passing the slip stream through a bed of coconut char-

coal, not only is the methane recovered, but also both nitrogen and carbon dioxide in the slip stream are vented and prevented from building up in the recycle gas. As a mixture of nitrogen, carbon dioxide, methane, and ethane was passed through a bed of coconut charcoal, a stream of nitrogen largely devoid of hydrocarbons passed out of the bed. As the adsorption was continued, the other components of the stream passed out of the bed in this order: methane, carbon dioxide, and ethane. When the bed became saturated with methane, methane began to pass out of the bed, and the charcoal bed was removed from service and replaced in service by a fresh charcoal bed. The components adsorbed on the saturated bed were desorbed with vacuum, in the order: methane, carbon dioxide, and ethane. Hence, by judicious use of vacuum, fractions rich in methane, carbon dioxide and ethane were isolated. The desorbed methane is returned back to the system, and nitrogen and carbon dioxide rejected, thus permitting a nearly complete return of methane to the system with high ultimate conversion and a minimal buildup of nitrogen and carbon dioxide in the system. With about a 20-minute adsorption of components from the slip stream and a 10-minute desorption of the adsorbed methane, a charcoal bed was able to be placed on a fast cycle for economic separation of components.

From the above description, it is apparent that the objects of the present invention have been achieved. While only certain embodiments have been set forth, alternative embodiments and various modifications will

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be apparent from the above description to those skilled in the art. These and other alternatives are considered equivalents and within the spirit and scope of the present invention.

Having described the invention, what is claimed is:

1. A method for converting at least one feedstock alkane containing from 1 to 3 carbon atoms to more valuable, heavier hydrocarbons, comprising:

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- (a) contacting the feedstock alkane containing from 1 to 3 carbon atoms with an oxygen-containing gas in a reactor in the presence of an oxidative coupling catalyst at a temperature in the range of from about 600° C. to about 1,000° C., to thereby produce a gaseous mixture comprising any remaining unreacted feedstock alkane and oxygen and saturated and unsaturated aliphatic hydrocarbon products having higher molecular weights than the feedstock alkane from which they were formed, wherein the oxidative coupling catalyst comprises silica free of a reducible metal compound and having a surface area of from about 5 m<sup>2</sup>/gm to about 175 m<sup>2</sup>/gm and
- (b) contacting the resulting gaseous mixture with an oligomerization catalyst under aromatization conditions to thereby produce a gaseous mixture comprising any remaining unreacted feedstock alkane and oxygen and an aromatic product and a saturated aliphatic hydrocarbon product having a higher molecular weight than the feedstock alkane from which it was produced, wherein the oligomerization catalyst comprises a solid having acidic sites and comprising a molecular sieve, a pillared smectite or vermiculite clay or a combination thereof, or a combination thereof with an amorphous refractory inorganic oxide.
2. The method of claim 1 comprising additionally:
- (d) recycling to step (1) at least a portion of at least the remaining unreacted feedstock alkane component of the gaseous mixture produced in step (b).
3. The method of claim 2 comprising additionally:
- (c) after step (b) and prior to step (d), separating at least the aromatic product from the gaseous mixture produced in step (b).
4. The method of claim 3 wherein the oxygen-containing gas comprises air, the gaseous mixture remaining after steps (a) and (b) comprises additionally nitrogen and carbon dioxide, and the gaseous mixture remaining after step (c) comprises nitrogen, carbon dioxide, any remaining unreacted feedstock alkane and oxygen and, if not separated in step (c), the higher molecular weight saturated aliphatic hydrocarbon product.
5. The method of claim 4 comprising additionally:
- (e) separating at least a portion of the nitrogen and carbon dioxide components from at least a portion of the gaseous mixture remaining after step (c), and then recycling the remaining unreacted feedstock alkanes in such portion of the gaseous mixture to step (a).
6. The method of claim 3 wherein the feedstock alkane comprises methane, wherein ethane and ethylene are produced in step (a) and wherein additionally at least a portion of any ethane component of the gaseous mixture remaining after step (c) is recycled to step (a), wherein at least a portion of the recycled ethane is converted to ethylene.
7. The method of claim 5 wherein the feedstock alkane comprises methane, wherein ethane and ethylene are produced in step (a) and wherein additionally at least a portion of any ethane component of the gaseous mixture remaining after step (c) is recycled to step (a), wherein at least a portion of the recycled ethane is converted to ethylene.
8. The method of claim 1 wherein step (a) is performed at a temperature in the range of from about 700° C. to about 850° C.

9. The method of claim 1 wherein step (a) is performed under a total pressure in the reactor in the range of from about 1 atm. to about 10 atm.

10. The method of claim 1 wherein the ratio of the combined feedstock alkane partial pressure-to-the oxygen partial pressure at the entrance to the reactor in step (a) is in the range of from about 2:1 to about 40:1.

11. The method of claim 1 wherein step (a) is performed at a space velocity of from about 100 to about 10,000 volumes of total feed gas per volume of catalyst per hour.

12. The method of claim 1 wherein step (b) is performed at a temperature in the range of from about 50° C. to about 500° C.

13. The method of claim 1 wherein step (b) is performed at a total absolute pressure in the range of from about 1 atm. to about 10 atm.

14. The method of claim 1 wherein step (b) is performed at a space velocity in the range of from about 100 to about 5000 volumes of gas per volume of catalyst per hour.

15. The method of claim 1 wherein the molecular sieve comprises a crystalline aluminosilicate, crystalline, borosilicate, or de-aluminated crystalline aluminosilicate, or mixture thereof, in the unexchanged or cation-exchanged form, or a combination thereof with an amorphous refractory inorganic oxide.

16. The method of claim 15 wherein the crystalline aluminosilicate comprises natural or synthetic chabazite, mordenite, erionite, clinoptilolite, zeolite A, zeolite L, zeolite X, zeolite Y, ultrastable zeolite Y, zeolite omega, ZSM-5, ZSM-11, ZSM-12, ZSM-35, ZSM-38 or ZSM-48.

17. The method of claim 16 wherein the crystalline aluminosilicate is in the hydrogen- or rare earth-exchanged form.

18. The method of claim 16 wherein the crystalline borosilicate molecular sieve comprises a molecular sieve material having the following composition in terms of mole ratios of oxides:



wherein M is at least one cation having a valence of n, y is between 4 and about 600, and z is between 0 and about 160, and providing an X-ray diffraction pattern comprising the following X-ray diffraction lines and assigned strengths:

d (Å)	Assigned Strength
11.2 ± 0.2	W-VS
10.0 ± 0.2	W-MS
5.97 ± 0.07	W-M
3.82 ± 0.05	VS
3.70 ± 0.05	MS
3.62 ± 0.05	M-MS
2.97 ± 0.02	W-M
1.99 ± 0.02	VW-M

19. The method of claim 1 wherein the solid comprises from about 5 to about 95 weight percent of an aforesaid refractory inorganic oxide and from about 5 to about 95 weight percent of an aforesaid molecular sieve or pillared smectite or vermiculite clay.

20. The method of claim 1 wherein the solid comprises (a) either silica, alumina or silica-alumina, and (b) either synthetic mordenite, ZSM-5, zeolite Y, ultrastable zeolite Y, pillared smectite or vermiculite clay or a crystalline borosilicate molecular sieve.

21. The method of claim 20 wherein the solid comprises alumina and either synthetic mordenite, ZSM-5 or a crystalline borosilicate molecular sieve.

\* \* \* \* \*

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**UNITED STATES PATENT OFFICE**  
**CERTIFICATE OF CORRECTION**

Patent No. 4,754,091 Dated June 28, 1988

Inventor(s) James L. Jezl, Glenn O. Michaels and Michael J. Spangler

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

<u>Patent</u> <u>Column</u>	<u>Line</u>	
1	45	Reads "arrives" and should read --arrive--.
2	3	Reads "zironia" and should read --zirconia--.
5	68	Reads "boriaalumina" and should read --boria-alumina--.
11	51	Reads "as a" and should read --at a--.
18	12	Reads "Selecitvity" and should read --Selectivity--.
21	Table 13	Reads "Product Selectivity 5.6 4.5" and should read --Product Selectivity--.
25	60	Reads "products" and should read --products.--

UNITED STATES PATENT OFFICE  
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Page 2 of 2

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It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

<u>Patent</u> <u>Column</u>	<u>Line</u>	
30	50	Reads "Speed Velocity" and should read --Space Velocity--.
34	22-23	Reads "crystalline, borosilicate" and should read --crystalline borosilicate--.

Signed and Sealed this  
Eleventh Day of April, 1989

*Attest:*

DONALD J. QUIGG

*Attesting Officer*

*Commissioner of Patents and Trademarks*